Tyco Laboratories, Inc.
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# THICK FILM SILICON GROWTH TECHNIQUES

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Sixth Quarterly Progress Report
Subcontract No. 953365
Covering Period: 1 June 1973 - 31 August 1973

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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## ABSTRACT

During this quarterly report period, considerable effort was directed toward finding an improved die material. Wetting experiments were conducted with various materials to determine their compatibility with silicon. Work has also continued toward the development of quartz as a die material as new techniques have provided more optimistic results than observed in the past.

As a result of the thermal modification described in the last quarterly report, improvements in growth stability have contributed to an increase in ribbon quality.

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## I. SUMMARY

Wetting experiments with various oxides, quartz carbon mixtures, and quartz carbon silicon nitride mixtures were conducted to determine the feasibility of any of these materials for use as dies.

New ideas and new techniques are being applied to quartz dies in an effort to fill the capillary and initiate growth. We feel that if this could be accomplished, wetting would occur and growth would be possible. Efforts to prefill the capillary and orifice have been conducted to gain this end.

Due to the thermal modifications, as described in the Fifth Quarterly Report, and to the addition of a new pulling mechanism, improvements in growth stability and quality have been achieved.

## II. INTRODUCTION

One primary limitation to the large-scale use of silicon solar cells in generating electric power from sunlight has been the lack of an industrially feasible process for the growth of single crystal silicon ribbons directly and continuously from the melt. Edge-defined, film-fed growth (EFG) is a process by which single crystals may be grown with their shape controlled by the outside dimensions of a die, the growth actually occurring through a thin liquid film on the top surface of the die.[1-5] The EFG method overcomes the need for refined temperature control during growth which characterized other attempts at the growth of ribbon-shaped crystals. However, the process imposes stringent requirements on the nature of the die material if semiconductor quality crystals are to be grown.

Fig. 1 illustrates the application of the EFG method to the growth of a ribbon-shaped crystal. When the crucible and melt are heated to above the melting point of silicon, the liquid silicon rises to fill the feeding slot by capillary action. A silicon seed crystal is then brought into contact with the liquid silicon in the capillary seed slot. After adjustment of the melt temperature and seed withdrawal rate, the molten silicon spreads across the top of the die until the spreading of the liquid silicon is halted by the 90° change in effective contact angle at the outer perimeter. The growth of a silicon crystal ribbon from the thin liquid meniscus shown in Fig. 1 is then established. This method has been applied to the growth of ribbons, filaments, tubes, and other shapes of sapphire, barium magnesium titanate, lithium fluoride, copper-gold alloy crystals, and beta-alumina, as well as to the directional solidification of a variety of eutectic materials.

The basic features of the EFG technique can be summarized as follows:

1. It produces accurately controlled cross sections and, in particular, thin ribbons can be produced directly.

2. It is self-stabilizing over a relatively wide range of power input fluctuations by means of changes in the thickness of molten film, or meniscus.

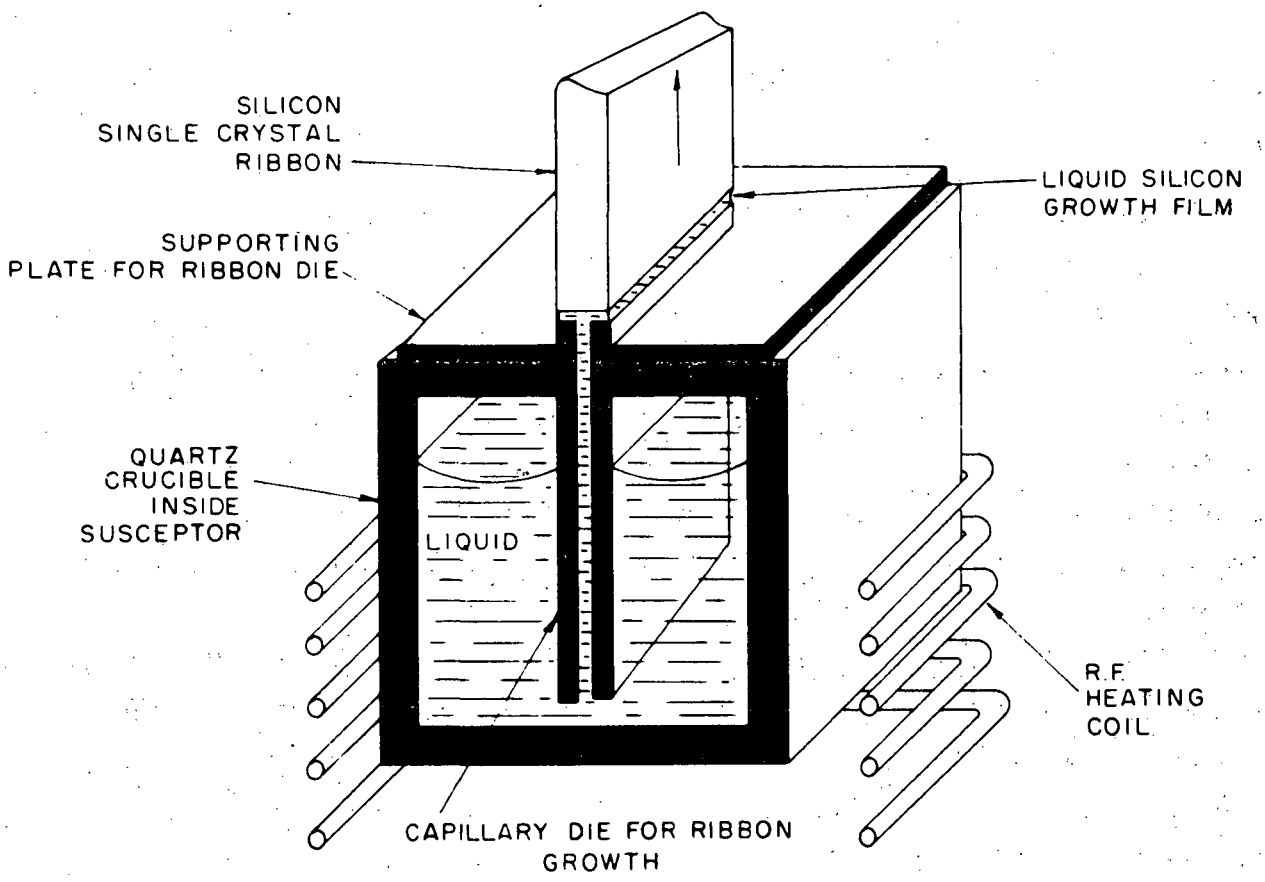


Fig. 1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon

3. Growth rates can be very fast since they are limited only by latent heat removal from the solid-liquid interface.

4. The growth interface is effectively decoupled from the bulk melt surface, permitting continuous replenishment of the melt during growth.

5. The crystal orientation can be arbitrarily chosen.

6. Because of the fast growth rate and the faster linear motion rate of the liquid supply, segregation effects tend to be completely overcome, and the crystallizing solid has the same average composition as the bulk liquid.

7. The steep thermal gradient between the growth interface and the die prevents the breakdown of planar growth. Thus, crystal perfection is enhanced and cellular substructure suppressed.

In the following sections of this report, we discuss the progress which has been made to date in applying this method to the thick film silicon ribbon growth.

## III. TECHNICAL DISCUSSION

### A. Ribbon Growth

As a direct result of the thermal modifications described in the previous report, significant improvements in growth stability have been observed during this period. This can be seen at the growth interface during spreading and then while maintaining full width for the duration of a run. The spreading has been uniform towards both edges and has been easily controlled by slow increases in pull speed until full width is achieved. To maintain the growth at full width, the pull speed can be held constant and only slight changes in temperature are required.

The interface profile has also been improved, as evidenced by these runs. In most cases, it has been flat. There have also been some ribbons where the curvature is slightly positive at the ends. Modifications to the shields and orifice curvature are still in progress to finally overcome this parameter. Fig. 2 is an example of what can be produced with the improved conditions. This particular ribbon is 28 in. long at full width. It was grown at 0.9 in./min and was grown the full length of the puller stroke. During growth, the speed was kept constant and only the temperature was varied. Also during growth, the puller was observed to be hesitating periodically. These hesitations almost caused freezing at a number of points in the growth. The areas show up as lines across the ribbon perpendicular to the growth direction. When the hesitations occur, SiC particles are picked up all along the interface, and these plus the new particles forming cause an increase in the longitudinal striations. Figs. 3 and 4 are Laué scans of the ribbon taken at the start of the full width portion and down further at 11 in. They show this portion to be essentially single crystal, although heavily dislocated. At the midpoint of the growth, the longest hesitation in pull speed almost caused total freezing. It was at this point that the ribbon went polycrystalline.

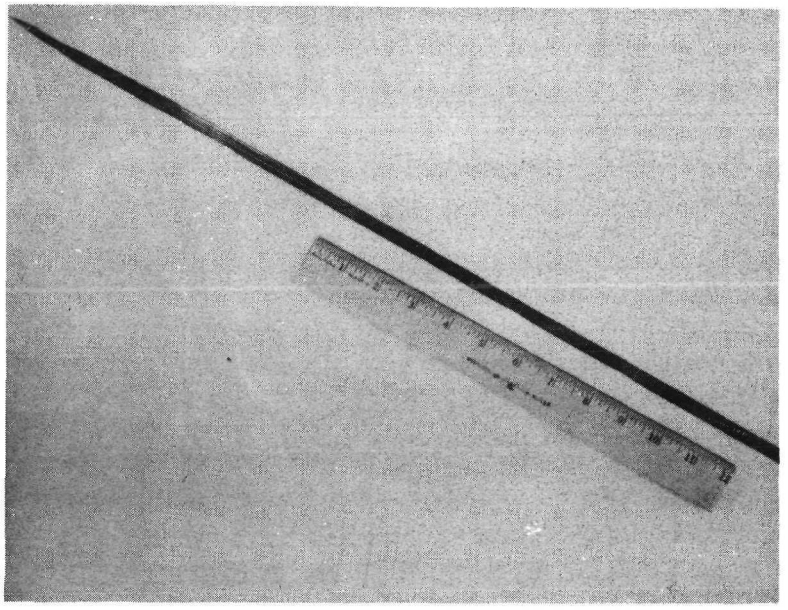

Fig. 2. Growth No. 168 resulting from thermal modifications. Single crystal from start to full width portion to midpoint of growth

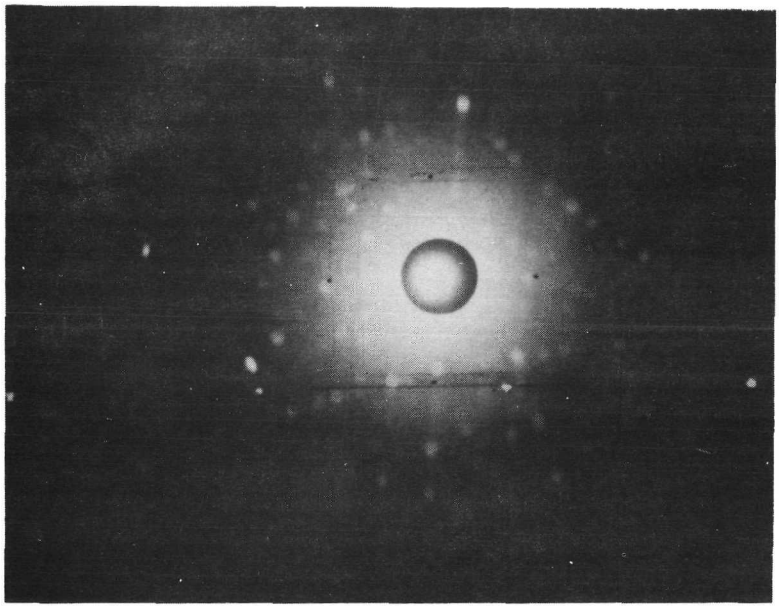

Fig. 3. Laué scan taken 2 in. in from the starting point of the ribbon shown in Fig. 2

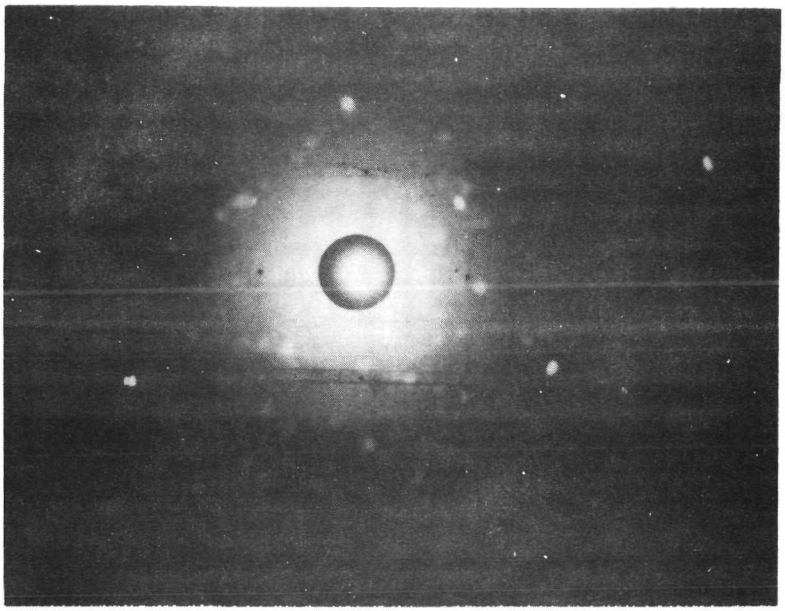

Fig. 4. Laué scan taken 2 in. in from the midpoint of the ribbon shown in Fig. 2

Figs. 5 and 6 are Laué pictures of another ribbon grown under these conditions. Although the length of this ribbon is not as dramatic, the crystallographic quality is still an improvement over past attempts. Fig. 5 shows the ribbon surface normal to the X-ray beam and Fig. 6 shows the same ribbon rotated in the beam 6° left on the horizontal plane and 11° off the vertical plane.

Attempts to grow thinner ribbons were also conducted and a design modification to the orifice was tried. The modification consisted of an increased bevel from 30 to 70°. The top capillary thickness was decreased to 0.004 in., giving a total thickness of 0.010 in. growth surface. These attempts have not been successful up to now, but there is some doubt as to the reason. While these tests were being conducted, the pulling mechanism was not working properly and could have been the cause of the failure.

In the last quarterly report, mention was made that a possible reduction of the amount of SiC precipitate could be gained at the orifice. This was to be accomplished by the elimination of overheating needed to fill the capillary with silicon. The suggestion made was to bring the setup to growth temperature and allow it to stand until the orifice filled. This method was tried and was successful in that the capillary did fill after approximately 20 min at growth temperature, and no overheating was needed. Unfortunately, no reduction was noted in the precipitate buildup.

B. Wetting Experiments

Wetting/compatibility experiments were conducted with $ThO_2$, $Y_2O_3$, AlN, $ZrO_2$ (CaO stabilized), $ZrO_2$ ($Y_2O_3$ stabilized), 80% $Si_3N_4$ + 10% $SiO_2$ + 10% graphite, and 90% $SiO_2$ + 10% graphite. Small chips of Si were melted on the surface of the test samples and held at approximately 1450°C for 30 min under an inert atmosphere. The samples were subsequently mounted, sectioned, polished, and examined grossly and microscopically.

The quartz/graphite mixture showed excellent wettability. Closer examination revealed substantial amounts of SiC in the Si layer covering the outside of the sample coupon, although there was relatively little penetration. It appears that lower amounts of graphite may be able to produce adequate wetting with less SiC formation.

The mixture of $Si_3N_4/SiO_2$/graphite showed reasonable wetting behavior. The solidified Si droplet had a contact angle of about 130 to 140°. The convention used here designates 0° as non-wetting and 180° as complete wetting. The entire surface of the sample also seemed to be wetted with Si. When sectioned, this turned out to be the result of the sample being completely infiltrated with Si. There did not appear to be any significant dissolution of the material, however. A few small SiC crystals

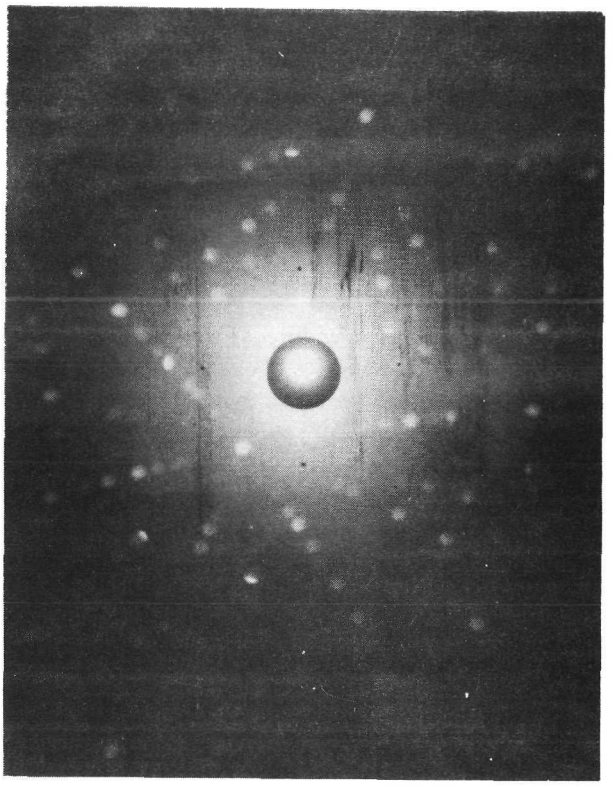

Fig. 5. Laué scan of ribbon No. 170-A 1/2 in. in from start

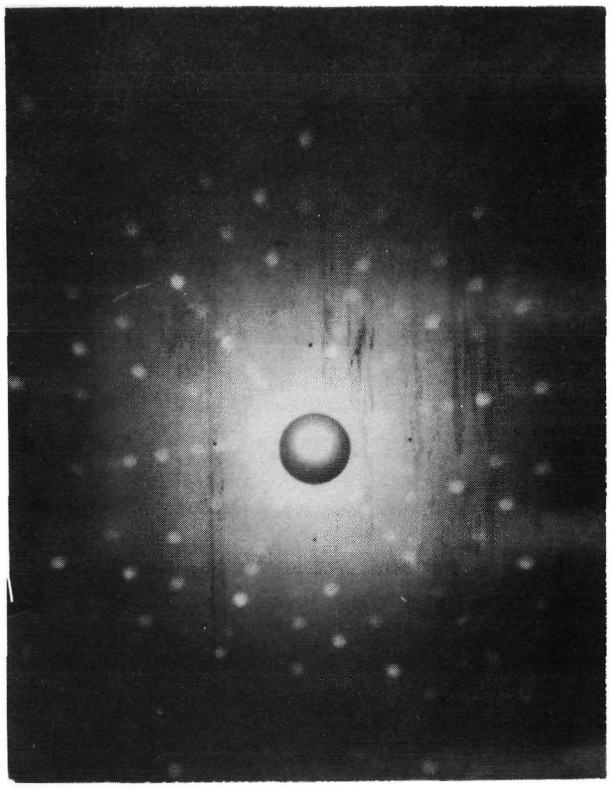

Fig. 6. Laué scan of ribbon No. 170-A 1 in. in from end

were found in the Si droplet, and a small, horizontal band of acicular crystals was found a short distance below the top of the Si. These are probably $Si_3N_4$, since this needle-like habit has been previously described for $Si_3N_4$ forming in liquid Si.[6] The total amount of dissolved and reprecipitated SiC and $Si_3N_4$ found throughout the Si is remarkably small considering the large surface exposed to molten Si. Possibly $Si_3N_4$ is significantly less soluble than SiC, although the findings of Kocher and Muhlbauer,[7] seem to indicate this is not the case. The behavior of this sample is intriguing and merits further consideration of this material and similar mixtures.

Aluminum nitride appeared to be a very well-behaved material -- wetting was positive, but confined to the areas of contact with the silicon. Microexamination, however, showed a zone of penetration of about 0.1 mm into the surface of the sample and substantial quantities of a two-phase material in the grain boundaries of the silicon. Fig. 7 shows these features. The grain boundary phase is probably Al-Si eutectic since it appears to have occurred as a liquid after solidification of the bulk of the silicon.

All four of the refractory oxides exhibited similar characteristics with molten silicon. Microphotographs of three are presented below. The fourth, zirconia, with calcium oxide as a stabilizer, behaved much like the yttria-stabilized zirconia, with the exception that large amounts of a glassy, probably calcium silicate, material formed, encapsulating the entire sample. Otherwise, it seems possible to discuss the materials as a group, since microexamination of the samples indicates similar behavior by all three. It appears that the molten silicon reduces the oxides and forms a silicide with the metal, which is then found as a eutectic with the silicon. The presence of a fourth phase, which in at least one case appears somewhat transparent, seems to indicate that possibly a silicate of the refractory oxide is also formed utilizing some of the oxygen from reduction of the oxide (see Figs. 8 through 10).

If, in fact, this happens, then there may be a possibility for stable two-phase equilibrium between the silicate and silicon. Examination of the phase diagrams between the refractory and rare-earth oxides and silica shows the existence of a number of congruently melting, and presumably stable, silicates of the form $MeSiO_4$ or $Me_XO_Y \cdot SiO_2$. Investigation of the stability of some of these compounds with liquid Si is definitely called for.

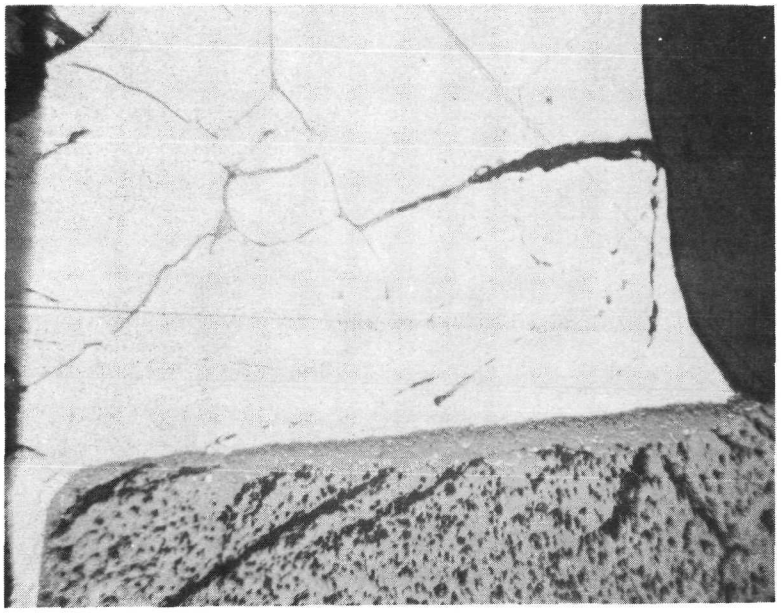

Fig. 7. Aluminum nitride/silicon compatibility test [AlN is at bottom of picture, a zone of penetration on the outer surface of the AlN is obvious as is a significant amount of two-phase material in the grain boundaries of the Si (70 X)]

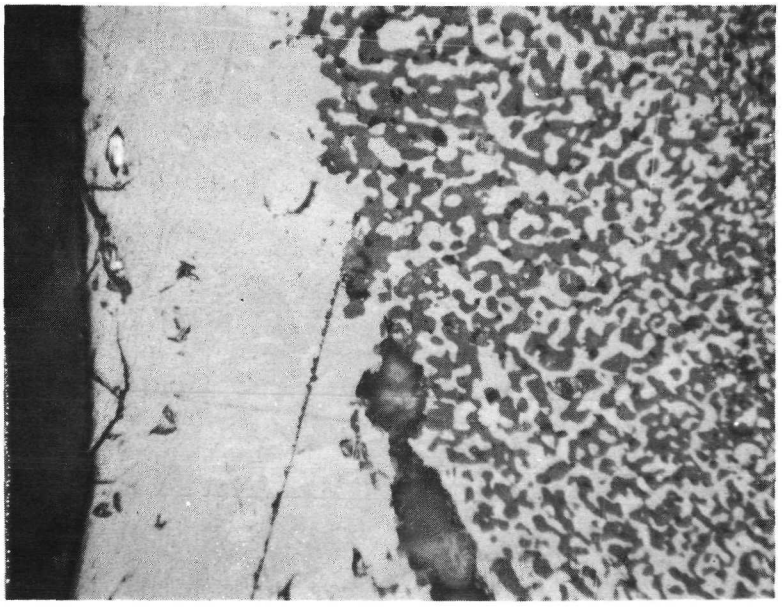

Fig. 8. Zirconium oxide (yttrium oxide stabilized)/silicon compatibility test [Right side of photo is skeleton of zirconia penetrated by silicon. To the left is the silicon in a eutectic mixture with a third phase. Small crystals of a fourth phase can be seen near the interface and near the surface of the silicon (70 X)

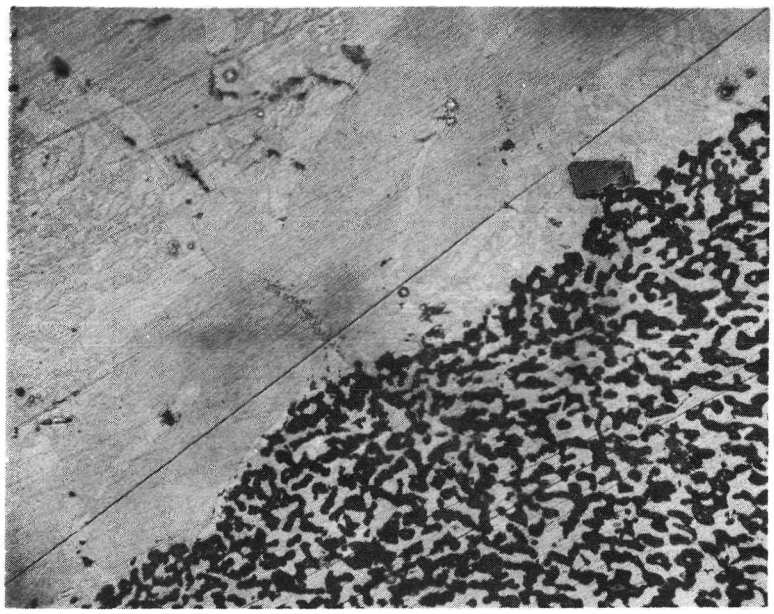

Fig. 9. Yttrium oxide/silicon compatibility test [Significant penetration and erosion of the yttria has taken place with subsequent formation of two new phases, one occurring as scattered, blocky crystals like that at the upper right, and the other as an obvious eutectic with the silicon-left portion of photo (300 X)]

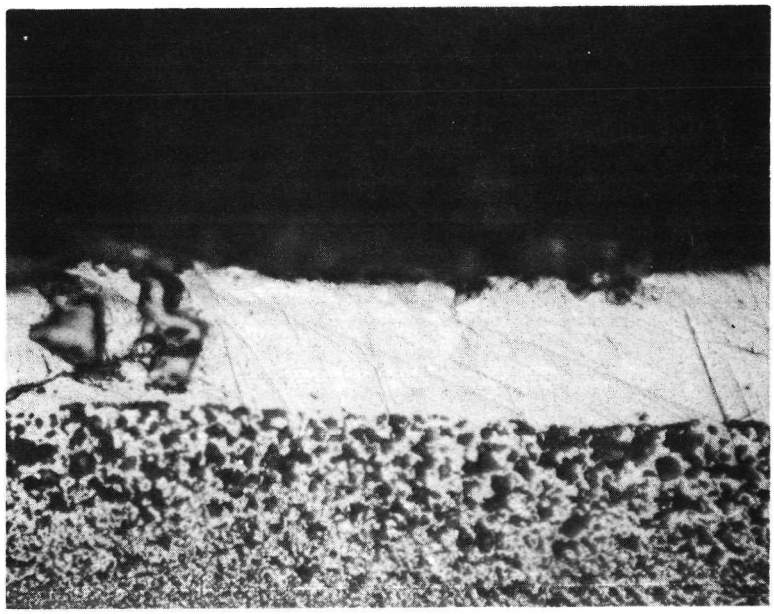

Fig. 10. Thorium oxide/silicon compatibility test [Behavior similar to yttria seems to have occurred here with the formation of a eutectic between the silicon and a new phase, and the formation of large blocky crystals of another phase (1000 X)]

C. Quartz Dies

After most growth attempts, there is some silicon left in the crucibles, and an inspection of these crucibles has shown evidence of wetting of the quartz by the silicon. We feel that after a period of time of contact between the two materials, wetting occurs. We have concluded that if the silicon could be brought up the capillary and held there until a growth could be started, wetting would occur, resulting in a continuous flow to the orifice.

To test this theory, a group of quartz dies were coated with silicon. Coatings 1000 Å and 5000 Å thick have been tried so far. In both cases, the silicon coating appeared to react with the quartz before capillary rise could take place. Further testing with thicker silicon coatings will be conducted in the near future.

Another approach attempted utilized a graphite wick. This consisted of a 0.006-in. thick graphite sheet 0.300 in. wide which was lowered down through the capillary of a quartz die into the melt. A 0.060 × 0.700-in. slot in the wick provided a graphite capillary. It was thought that the silicon would fill the slot in the graphite; then, as the wick was withdrawn, it would draw silicon up the quartz capillary and be held there until wetting took place. Unfortunately, no capillary rise took place in the graphite wick, and as it was withdrawn, contact with the melt was lost. This method does not appear feasible due to these results.

Two other approaches are also being investigated at this time, and although no ribbons have been produced as yet, we have obtained some positive results.

The first method makes use of a floating quartz orifice. Although this is the least practical of the two methods, it can be quickly made in the lab. This provides a fast method for determining the thermal shielding configuration needed which will be identical to that required for the second method. The orifice consists of a quartz disc with a 0.015 in. × 0.500 in. slot cut through the center and with its edge curled up forming a flat bottomed shallow disc. The weight of the disc floating on the surface of the melt pushes molten silicon into the slot which is the orifice. A series of experiments has been conducted with this type of orifice, and the problems encountered thus far have been the unpredictable positioning of the orifice with respect to the viewport and the thermal gradients necessary to sustain growth. When the thermal gradient problem is solved and a growth obtained, a similar shield arrangement will be applied to the other method.

This method uses a similar orifice but is fixed in position. It uses the same type of disc and slotted quartz with a supporting flange attached. Two capillary plates are attached on the bottom of the slot spaced 0.060 in. apart. During a growth attempt, the orifice sits on the surface of the melt and the capillary within it. With this configuration, the capillary and orifice are filled with silicon as soon as melting occurs. If the silicon does adequately wet the quartz after a period of time, then as the melt level starts to drop, capillary action should provide a continuous flow to the orifice sustaining growth.

Tests are continuing with the floating orifice, and a delivery of the second type is expected shortly.

D. Pulling Mechanism

The new puller has been installed and has significant advantages over the old machine. A higher torque motor and more rigid pull rod contained within a bellows are the two most important features. The higher torque of the motor has eliminated the hesitation, resulting in a continuous pull, and there is less chance of freezing as well as less SiC particles picked up in the ribbon because of this. The more rigid pull rod has substantially reduced vibration transmitted from this pulling mechanism, contributing to a reduction of effects caused by the SiC as there will be less chance of the ribbon to brush back and forth into the precipitate.

## IV. NEW TECHNOLOGY

No new developments are to be reported during this contracting period.

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## V. CONCLUSIONS AND RECOMMENDATIONS

Work will continue towards gaining a proper thermal gradient for growth with a floating quartz orifice. This data will be applied to the fixed orifice where growths should also be obtained. Once growths have been obtained and if wetting occurs, crystallographic quality is good, and die life is reasonable, then the use of quartz dies would be a very real possibility.

The wetting experiments have shown that $SiO_2$ mixed with smaller amounts of silicon nitride and carbon will wet. There is also some evidence that there may be a class of stable compounds of refractory silicates which could be used. Wetting tests will continue on new materials, and dies will be made from those which show promise. Dies will also be made and tested with quartz carbon and quartz carbon silicon nitride mixtures.

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